SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 205.1

DETERMINATION OF HEXAVALENT CHROMIUM AND TOTAL CHROMIUM EMISSIONS FROM CHROME PLATING AND ANODIZING EQUIPMENT USING A WET IMPINGEMENT TRAIN

TECHNICAL SUPPORT SERVICES
APPLIED SCIENCE AND TECHNOLOGY
AUGUST 1991

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TABLE OF CONTENTS

3. Laboratory Procedures

3.1 Apparatus

3.2 Reagents

3.3 Pretest Preparation

3.4 Preparation of Sample Collection Train

3.5 Leak Check

3.6 Sample Recovery

3.7 Sample Analysis

3.8 Calculation and Reporting

3.9 Calibration

3.10 Quality Control

4. Engineering Calculations and Reporting

4.1 Sample Volume

4.2 Concentration

METHOD 205.1

DETERMINATION OF HEXAVALENT CHROMIUM AND TOTAL CHROMIUM EMISSIONS FROM CHROME PLATING AND ANODIZING EQUIPMENT USING A WET IMPINGEMENT TRAIN

Section 1 of 4

1. Overview

1.1 Principle

A sample of stack gases is withdrawn isokinetically from the source through a wet impingement train. The chromium aerosol is collected in impingers containing 0.02N $NaHCO_3$ solution, and also by a backup Teflon filter. Aliquots of the collected sample are analyzed for hexavalent chromium and the remainder is digested and analyzed for total chromium.

The hexavalent chromium analysis is performed with a visible range spectrophotometer by the diphenylcarbazide (DPC) method. If the absorbance measured for any sample by the DPC method is less than 0.010, then use the ion chromatography (IC) method. (The hexavalent chromium concentration which corresponds to this

absorbance level will vary with different spectrophotometers, but is approximately 0.01 ppm with a Perkin-Elmer Model 552A with a one-centimeter solution path length.)

The remainder of the sample is prepared for total chromium analysis by an acid digestion procedure. The total chromium analysis is performed with an atomic absorption spectrophotometer (AAS) in the flame mode, using a nitrous oxide-acetylene flame. If the absorbance measured for any sample by this flame-AAS method, at an absorption wavelength of 357.9 nm, is less than 0.100, then use the furnace-AAS method. (The total chromium concentration which corresponds to this absorbance level will vary with different spectrophotometers, but is approximately 0.1 ppm with a Varian SpectrAA-40 burning with a rich red flame.)

1.2 Applicability

This method is used to determine total chromium and hexavalent chromium (Cr^{6+}) emissions from chrome plating and anodizing operations. See Interferences for the method limitations.

Application of this method may be extended and variations may be used with the approval of the Executive Officer.

1.3 Range and Precision

1.3.1 Hexavalent Chromium by DPC Method

The response curve is a straight line in the 10 to 200 ng/mL range of hexavalent chromium. A minimum detection limit of 10 ng/mL has been observed. For a minimum analytical accuracy of ± 10 percent, the lower limit of the range is approximately 20 ng/mL. The upper limit can be extended by appropriate dilution.

1.3.2 Hexavalent Chromium by IC Method

A straight line response curve can be obtained in the 5 to 50 ng/mL range of hexavalent chromium. With direct injection of 250 µL, the minimum detection limit is approximately 1 ng/mL. Preconcentration of a larger sample will lower the detection limit correspondingly. A quantifiable limit of 6 pg/mL using

preconcentration of a 20 mL aliquot has been reported.

1.3.3 Total Chromium by Flame-AAS Method

Using the most sensitive wavelength for chromium of 357.9 nm, the working range is 0.1 to 50 μg/mL of chromium. Using less sensitive wavelengths, e.g. 425.4 nm, 428.9 nm, 520.8 nm, and 520.4 nm, direct measurements without dilutions may be made for much higher concentrations of chromium. The optimum working range for each of these wavelengths has not been determined for the nitrous oxide-acetylene flame, but is expected to extend as high as 6000 ppm chromium for the least sensitive wavelength.

1.3.4 Total Chromium by Furnace-AAS Method

The analytical working range is 1 to 20 ng/mL, using 20 μL injections in an argon atmosphere.

1.4 Interferences

1.4.1 Interferences for Hexavalent Chromium by DPC Method

Molybdenum, mercury, and vanadium react with diphenylcarbazide to form a color. However, approximately 200 µg/mL of these elements can be present in a sample without creating a problem. Iron produces a yellow color, but this effect is not measured photometrically at 540 nm.

1.4.2 Interferences for Hexavalent Chromium by IC Method

Trivalent chromium is separated during the chromatography step, and will not interfere. Fe (III) produces a negative interference when it is present in concentrations greater than approximately 500 µg/mL.

1.4.3 Interferences for Total Chromium by Flame-AAS Method

No interferences are expected when a nitrous oxide-acetylene flame is used instead of an air-acetylene flame.

1.4.4 Interferences for Total Chromium by Furnace-AAS Method

The long residence time and high concentrations of the atomized sample in the optical path of the graphite furnace can result in severe physical and chemical interferences.

Furnace parameters should be optimized to minimize these effects. If the analyte is not completely volatilized and removed from the furnace during atomization, memory effects will occur. If this situation is detected, clean the tube by operating the furnace at higher atomization temperatures.

Do not use nitrogen as the purge gas to eliminate the possibility of cyanogen band interference.

Low concentrations of calcium may cause interferences. At concentrations above 200 µg/mL the effect is constant. Calcium nitrate may be added to ensure a known constant effect (optional).

1.4.5 Special Considerations

Since SO_2 reacts with Cr^{6+} on an approximately equimolar basis and converts it to Cr^{3+}, flue gases that contain SO_2 can create a substantial negative interference. The magnitude of the interference depends on their relative concentrations.

Hexavalent chromium may be lost due to reactions with organics or other oxidizable materials, or gained by use of contaminated equipment or reagents. Improper sample storage may lead to changes in sample concentrations. Because of these considerations, it is necessary to scrupulously clean all equipment, and follow all instructions on reagent purity and sample stabilization and storage, as described in this method. For the same

reason, prepare trains without using grease, since even small amounts will reduce hexavalent chromium.

METHOD 205.1

DETERMINATION OF HEXAVALENT CHROMIUM AND TOTAL CHROMIUM EMISSIONS FROM CHROME PLATING AND ANODIZING EQUIPMENT USING A WET IMPINGEMENT TRAIN

Section 2 of 4

2. Field Procedure

2.1 Sampling Apparatus

2.1.1 Sampling Train

A schematic of the sampling train used in this method is shown in Figure 205.1-1.

a. Probe Nozzle

The nozzle material shall be glass or quartz with a sharp, tapered leading edge. The taper angle shall be $\leq 30^{o}$ and on the outside, to preserve a constant internal diameter. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of

0.16 cm (1/16 in.), e.g. from 0.32 to 1.27 cm (1/8 to 1/2 in.) or larger if higher volume trains are used.

Each nozzle must be calibrated before its use. (See Method 5.1, Section 2.1.1 a.)

b. Probe Liner

Use borosilicate or quartz probe liners.

c. Pitot Tube

Use an S-type Pitot tube, as described in Section 1.1 of Method 2.1. Attach the Pitot tube to the probe as shown in Figure 205.1-1 for monitoring the stack gas velocity. Refer to Method 2.1 for the specifications of the assembly.

d. Differential Pressure Gauge

Use an inclined manometer or equivalent device, as described in

Method 2.1, for stack velocity head readings, and a separate manometer for orifice differential pressure readings.

e. Impinger Train

The train consists of four Greenburg-Smith design impingers connected in series with ground-glass fittings, or any similar leak-free non-contaminating fittings. The first and second impingers must be of the Greenburg-Smith design with the standard tip. The third and fourth impingers must be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (1/2 in.) ID glass tube extending to about 1.3 cm (1/2 in.) from the bottom of the flask. The first and second impingers contain 100 mL of 0.02N $NaHCO_3$. The third is empty, and the fourth contains a known weight of 6 to 16 mesh indicating-type silica gel or equivalent. Place a thermometer capable of measuring temperature to

within 1°C (2°F) at the outlet of the fourth impinger to monitor outlet gas temperature.

Instead of using silica gel the moisture leaving the third impinger may be determined by monitoring the temperature and pressure at the exit of the impinger train and then applying Dalton's law of partial pressures.

f. Filter Holder

Use a borosilicate glass filter holder, with a glass frit, Teflon, or stainless steel filter support. If a stainless steel filter support is used, protect the Teflon filter from the filter support by placing a glass fiber filter between the two.

g. Metering System

The metering system includes vacuum gauge, leak-free pump, thermometer capable of measuring temperature to

within 3°C (5.4°F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 205.1-1. An alternative to the thermometer and dry gas meter is an equivalent temperature-compensated dry gas meter. When the metering system is used in conjunction with a Pitot tube, the system should allow for checks of isokinetic rates.

2.1.2 Temperature Determination Equipment

Use the temperature sensor described in Method 2.1. Preferably, the temperature sensor should be permanently attached to the Pitot tube or sampling probe so that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch metal.

2.1.3 Barometer

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm (0.1 in.) Hg is used.

The barometric pressure may be obtained from a nearby National Weather Service (NWS) station. Request the station value (which is the absolute barometric pressure) and adjust for elevation difference between the NWS station and the sampling point at the rate of minus 2.5 mm (0.1 in.) Hg per 30 m (100 ft) elevation increase or plus the same adjustment for elevation decrease.

2.1.4 Gas Molecular Weight-Determination Equipment

Same as Method 3.1. Concurrent determination is not required when the process is steady state and molecular weight varies less than 2 percent.

2.2 Sampling Reagents

a. 0.02N $NaHCO_3$ Solution (Nominal)

See Section 3.2.1 d for preparation.

b. Filters

Teflon filters, 0.3 micron.
Glass fiber filters are needed when stainless steel filter supports are used.

c. Silica Gel

Indicating-type silica gel, 6 to 16 mesh.

Use new silica gel as received. If previously used, dry at 175°C (350°F) for 2 hours. Other types of desiccants may be used subject to the approval of the Executive Officer.

d. Water

e. Crushed ice or dry ice pellets.

2.3 Pretest Determination

Select the sampling site and the minimum number of sampling points according to Method 1.1. Determine the static pressure, temperature, and

the range of velocity heads using Method 2.1. Perform leak check of the Pitot lines (see Method 2.1).

With glass liners, install the selected nozzle using a Viton A O-ring. Other connecting systems using Teflon ferrules may be used. The use of one piece glass probe with nozzle will avoid the possibility of leaks. Mark the probe with heat resistant tape to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 205.1-1. Do not use grease on the ground-glass joints, or anywhere else in the sampling apparatus upstream of the filter, to preclude the possibility of contamination of the sample by the grease.

Place crushed ice or water and dry ice around the impingers.

Determine the moisture content of the stack gas using Method 4.1 or its alternative to make sampling rate settings. Determine the stack gas dry molecular weight as described in Method 2.1. In most of the cases, the dry molecular weight of

the effluent gases from chromium plating operations may be assumed to be 28.95. Select a nozzle size based on the range of velocity heads encountered, so that it is not necessary to change the nozzle to maintain isokinetic sampling rates. During the run, do not change the nozzle. Choose the proper differential pressure gauge for the range of velocity heads encountered (see Method 2.2).

Select a probe length suitable for sampling all traverse points. For large stacks, consider sampling from opposite sides of the stack (four sampling ports) to reduce probe length.

The total sample volume (corrected to standard conditions) must not be less than 180 cubic feet. The sampling time at each traverse point must be an integer or an integer plus one-half minute. The sampling time should be the same at each point.

2.4 Gas Volume Meter Check

See Method 5.1, Section 2.4.

2.5 Leak Checks

Follow the procedure as described in Method 5.1, Section 2.5.

2.6 Sampling Train Operation

Follow the procedure as described in Method 5.1, Section 2.6.

2.7 Calculation of Percent Isokinetic Flow

Calculate percent isokinetic flow using the equation shown in Method 5.1, Figure 5.1-6, to determine whether the run was valid or another test run should be made.

2.8 Sample Handling

Follow the procedure as described in Method 5.1, Section 2.8.

2.9 Calibration

See Chapter III.

DETERMINATION OF HEXAVALENT CHROMIUM AND TOTAL CHROMIUM EMISSIONS FROM CHROME PLATING AND ANODIZING EQUIPMENT USING A WET IMPINGEMENT TRAIN

3. Laboratory Procedures

3.1 Apparatus

3.1.1 Sampling Train

A schematic of the sampling train is shown in Figure 205.1-1.

See description in Section 2.1.

3.1.2 Sample Recovery

a. Wash Bottles

Polyethylene.

b. Balance

To measure to 0.5 g.

c. Sample Containers

Leak-free linear polyethylene bottles (LPE).

d. Funnel

Glass, to aid in sample recovery.

e. pH Meter

Capable of accurately measuring pH to 0.02.

3.1.3 Analysis

3.1.3.1 Apparatus for Hexavalent Chromium by DPC Method

a. Volumetric Flasks

A 50 mL volumetric flask for each sample, spike, blank, and standard; and one 100 mL and three 1000 mL flasks for reagent preparation.

b. Pipets

Assorted sizes, as needed.

c. Spectrophotometer

Double beam, visible range, capable of measuring absorbance at 540 nm.

3.1.3.2 Apparatus for Hexavalent Chromium by IC Method

a. Dionex* Single Channel Ion Chromatograph

P/N 37029 (or equivalent).

b. Dionex* HPIC-CG5 Cation Guard Column

P/N 37028, (or equivalent).

c. Dionex* HPIC-CS5 Cation Separator Column

P/N 37030, (or equivalent).

d. Dionex* Reagent Delivery Module (RDM)

P/N 35354, (or equivalent).

e. Dionex* Membrane Reactor

P/N 35354, (or equivalent).

f. Dionex* Visible Detector (VSM)

P/N 37044, (or equivalent).

g. Preconcentration Column

CG-5 (or equivalent).

h. pH Meter

See Section 3.1.2 e.

*Dionex is the trade name of an ion chromatograph manufactured by Dionex Corp. No endorsement of the company or its products is implied or intended.

3.1.3.3 Apparatus for Digestion for Atomic Absorption Analysis

a. Beakers

600 mL.

b. Filtration Apparatus

Consisting of all plastic and glass suction flask and filter holder.

c. Volumetric Flasks

50 mL.

d. Linear Polyethylene Bottles (LPE)

100 mL.

3.1.3.4 Apparatus for Total Chromium by Flame-AAS Method

a. Atomic Absorption Spectrophotometer

Single or dual channel, single-or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm and provision for simultaneous background correction.

b. Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp

c. Electric Heater for Nitrous Oxide Supply Line

d. Burner Suitable for Nitrous Oxide Acetylene Flame

3.1.3.5 Apparatus for Total Chromium by Furnace-AAS Method

a. Atomic Absorption Spectrophotometer

Single or dual channel, single-or double-beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190 to 800 nm and provisions for simultaneous background correction and interfacing with a strip chart recorder.

b. Chromium Hollow Cathode Lamp or Electrodeless Discharge Lamp

c. Graphite Furnace

Any graphite furnace device with the appropriate temperature and timing controls.

d. Strip Chart Recorder

A recorder is strongly recommended for furnace work so that there will be a

permanent record and so that any problems with the analysis such as drift, incomplete atomization, losses during charring, changes in sensitivity, etc., can easily be recognized.

3.2 Reagents

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. Where such specifications are not available, use the best available grade.

3.2.1 Reagents for Pretest Preparation and Sample Collection

a. Water

Water must meet ASTM Type I specifications or better, except that distilled water is not necessary as a feedstock. Where distilled water is not used, the deionizing system must also contain particulate filters,

carbon adsorption, and a UV light for sterilization. Reference to water throughout this method implies water as defined here unless expressly redefined.

b. Nitric Acid (HNO_3), Concentrated, Low Trace Metals

All subsequent references to HNO_3 mean low trace metal grade unless expressly redefined.

c. Nitric Acid (HNO_3), 1:1

Prepare by carefully adding one liter of concentrated HNO_3 in small increments to one liter of water while mixing.

d. Sodium Bicarbonate ($NaHCO_3$), 0.02N (Nominal)

Dilute 2 g of ultrapure $NaHCO_3$ to one liter with water.

e. Silica Gel

See Section 2.2.6.

3.2.2 Reagents for Sample Recovery

a. Sodium Bicarbonate ($NaHCO_3$), 0.02N (Nominal)

See Section 3.2.1 d.

b. Nitric Acid (HNO_3), 0.1N (Nominal)

Dilute 6.5 mL of concentrated HNO_3 to one liter with water.

3.2.3 Sample Analysis

3.2.3.1 Reagents for Hexavalent Chromium by DPC Method

a. Water

See Section 3.2.1 a.

b. Potassium Dichromate ($K_2Cr_2O_7$) Stock Solution

Dissolve 2.829 g of dried analytical reagent grade $K_2Cr_2O_7$ in water, and dilute to exactly one liter (1 mL = 1000 μg Cr^{6+}) with water.

c. Potassium Dichromate Intermediate Solution

Dilute 1.0 mL potassium dichromate stock solution to exactly one liter (1 mL = 1 μg Cr^{6+}) with water.

d. Potassium Dichromate Working Standards

Pipet 0, 1, 5, 10, 20, and 40 mL of dichromate standard solution (above) into 50.0 mL flasks and acidify each to pH 2.0 $\pm$ 0.5 with 1:1 HNO_3. Add 10 mL DPC and dilute to

exactly 50.0 mL with water. This corresponds to 0, 1, 2, 5, 10, 20, and 40 μg of hexavalent chromium.

e. Acetone, ACS Reagent Grade

f. Diphenylcarbazide Solution

Dissolve approximately one-half gram of 1,5-diphenylcarbazide (DPC) in approximately 100 mL acetone. Store in a brown bottle. Discard when the solution becomes discolored.

3.2.3.2 Reagents for Hexavalent Chromium by IC Method.

a. 2,6-Pyridinedicarboxylic Acid (PDCA)

b. Disodium Hydrogen Phosphate Heptahydrate

c. Sodium Iodide

d. Ammonium Acetate

e. Lithium Hydroxide Monohydrate

f. 1,5-Diphenylcarbazide (DPC)

g. Methanol, HPLC Grade

h. Sulfuric Acid, 96 Percent, Spectrophotometric Grade

i. Water

J. Degassed Water

Bubble helium though one liter of water for about 10 minutes.

k. Eluent Stock

Prepare by dissolving the following reagents in water.

(PDCA is slow to dissolve, and heating the solution before addition of the remaining reagents may be used to increase the rate of dissolution).

20.0 mM (3.34 g/L) Pyridinedicarboxylic Acid (PDCA)

20.0 mM (5.36 g/L) Disodium Hydrogen Phosphate Hepta-hydrate ($Na_2HPO_4 \cdot 7H_2O$)

100.0 mM (15.0 g/L) Sodium Iodide (NaI)

500.0 mM (38.5 g/L) Ammonium Acetate ($NH_4C_2H_3O_2$)

28.0 mM (1.18 g/L) Lithium Hydroxide Mono-hydrate ($LiOH \cdot H_2O$)

l. Eluent

Prepare by diluting 100 mL of the eluent stock to 1 liter with degassed water. The pH of the diluted eluent should be between 6.70 and 6.80. Use a pH meter for this preparation.

m. Post-Column Reagent

Prepare by dissolving 0.49 g of 1,5-diphenylcarbazide (DPC) in 100 mL of methanol. Add this solution to about 500 mL of degassed water containing 25 mL of concentrated sulfuric acid. Dilute to 1 liter with degassed water.

n. Potassium Dichromate Stock

Same as Section 3.2.3.1 b.

o. Potassium Dichromate Intermediate Solution

Same as Section 3.2.3.1.C.

p. Potassium Dichromate Working Standards

Make a five point calibration curve by diluting the potassium dichromate intermediate with water. The standards must bracket the lowest sample concentration, and the highest standard must not be more than 10 times the lowest standard.

3.2.3.3 Reagents for Total Chromium by Flame-AAS

a. Water

b. Chromium Stock Solution (1000 µg/mL)

Either procure a certified aqueous standard from a supplier (e.g., Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.829 g of dried $K_2Cr_2O_7$, analytical reagent grade) in water and dilute to exactly one liter (1 mL = 1000 μg Cr^{6+}).

c. Chromium Intermediate Solution

Dilute 10 mL of chromium stock solution above) to 100 mL with 2.5 percent (v/v) HNO_3 solution (1 mL = 100 μg Cr).

d. Chromium Working Standards

The working range of flame AAS is approximately 0.1 to 50 μg/mL. Prepare a minimum three point calibration curve. The lowest absorbance reading should be 0.01, and the linear

regression must have a correlation coefficient of 0.997 or better. For many instruments, this can be done by taking 1, 5 and 10 mL of intermediate, and diluting each to exactly 100 mL with 2.5 percent (v/v) HNO_3 solution. This corresponds to 1, 5 and 10 µg/mL. These standards must be made fresh daily.

e. Nitrous Oxide

f. Acetylene

3.2.3.4 Reagents for Total Chromium by Furnace-AAS Method

a. Water

b. Nitric Acid (HNO_3)

Low trace metal.

c. Hydrogen Peroxide (H_2O_2)

30 percent (optional).

d. Calcium Nitrate Solution (Optional)

Dissolve 11.8 g of calcium nitrate, $Ca(NO_3)_2 \cdot 4H_2O$, in water and dilute to one liter. If the instrument manufacturer recommends a different matrix modifier, then use that reagent.

e. Chromium Stock Solution (1000 µg/mL)

Either procure a certified aqueous standard from a supplier (e.g., Spex Industries, Alpha Products, or Fisher Scientific) and verify by comparison with a second standard, or dissolve 2.829 g of dried potassium dichromate ($K_2Cr_2O_7$, analytical reagent

grade) in water and dilute to exactly one liter (1 mL = 1000 µg Cr).

f. Chromium Intermediate Standard Solution (A)

Take 10 mL of chromium stock solution and dilute to exactly one liter with water (1 mL = 10 µg Cr).

g. Chromium Intermediate Standard Solution (B)

Take 10 mL of chromium intermediate (A) and dilute to exactly one liter with 2.5 percent (v/v) nitric acid solution (1 mL = 100 ng chromium).

h. Chromium Working Standards

The working range of furnace AAS is approximately 1 to 20 ng/mL. Most furnaces pipet

automatically. They adjust the volume of the injected solution standard to generate a calibration curve. Prepare a 20 ng/mL standard by taking 20 mL of chromium intermediate (B), and diluting to exactly 100 mL with 2.5 percent (v/v) HNO_3 solution. Make fresh daily.

In addition, 1 mL of 30 percent H_2O_2 and 1 mL of calcium nitrate may be added to lessen interferences.

3.3 Pretest Preparation

All sampling and analytical containers which come in contact with the sample must be thoroughly cleaned with detergent and water, and rinsed thoroughly with tap and deionized water. Soak non metal parts in 1:1 HNO_3 for at least one hour, rinse thoroughly with water, and allow to air-dry (this includes the probe liner, sample lines and impinger connectors, impingers, sample containers and beakers, filtration apparatus,

watch glasses, pipets, etc). Rinse metal parts (such as the nozzle and filter holder) with 1:1 HNO_3 and water, and allow to air-dry. Protect the equipment from contamination by closing all the openings with clean plastic caps.

3.4 Preparation of Sample Collection Train

During the preparation and assembly of the sampling train, keep all openings covered, until just prior to assembly.

Assemble the impingers in the train as shown in Figure 205.1-1. Place about 100 mL of 0.02N $NaHCO_3$ in each of the first two impingers. Leave the third impinger empty. Place approximately 200 to 300 g of silica gel in the fourth impinger and record its weight to the nearest 0.5 g.

Do not use grease on the impinger joints, or anywhere else in the sampling train upstream of the filter, to preclude the possibility of contamination of the sample with grease, which interferes severely with hexavalent chromium analysis.

If moisture content is to be determined gravimetrically, weigh each impinger plus its contents to the nearest 0.5 g and record the weights.

Using a tweezer or clean disposable surgical gloves, place the Teflon filter in the filter holder. If the filter support is made of stainless steel, protect the sample filter from the support by first placing a glass fiber filter on the support. Be sure that the filter(s) are properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Assemble and tighten the filter holder. Connect the impingers and filter holder as shown in Figure 205.1-1, using glass, Teflon, or polyethylene tubing.

Prepare a blank train using the same procedure as above.

3.5 Leak Check

The sample collection train may be leak checked in the laboratory after assembly using the procedure in Section 2.5.

3.6 Sample Recovery

The sample must be recovered within a few hours of sampling, as overnight storage can lead to significant sample degredation. Furthermore, it is strongly recommended that the intact and secured train be delivered to the laboratory for recovery. On recovery, inspect the train for general condition. Note if the silica gel is expended, or any unusual conditions that may affect results.

Recover the sample in an area protected from the wind and free from dust and possible contamination by chromium or organic materials. Wipe the outside of the train components to prevent any contamination of the sample. Disconnect the train components. Weigh each impinger plus contents to the nearest 0.5 g and record these weights.

Transfer the impinger contents to an acid-washed linear polyethylene (LPE) sample container, tared to the nearest 0.1 g. Using the minimum necessary for quantitative recovery, rinse the nozzle, probe liner, impingers, and connectors with 0.02N $NaHCO_3$ at least three times. Add

these rinses to the sample container. Check the pH of the $NaHCO_3$ fraction with a pH meter. Adjust to pH 7 to 8 using 1:1 HNO_3. Record the total weight of the recovered sample to the nearest 0.1 g. Make a final 0.1N HNO_3 rinse of the sampling equipment, and pour it into another acid-washed LPE container (this fraction is also analyzed for total chromium).

Carefully remove the sample (Teflon) filter from the filter holder, and insert it into the $NaHCO_3$ fraction. Discard the glass fiber filter if it was used to shield the Teflon filter from a stainless steel filter support. Seal the container and mix well. Mark the liquid level on the container and label it to identify its contents. Refrigerate at $4^{o}C$ until analysis.

Recover the blank train using the same procedure.

3.7 Sample Analysis

3.7.1 Hexavalent Chromium by DPC Method

Inspect the sample container to determine if a noticeable amount of liquid has been lost. If it has, either void the sample

or correct the results using methods approved by the Executive Officer.

First calibrate the spectrophotometer as described in Section 3.9.1. Take two 40.0 g aliquots of the sample in 50 mL volumetric flasks. This can be done by pouring from a beaker into the tared flask, and adding drops with a plastic eyedropper until the 40.0 g shows on the balance. One aliquot is used for analysis and the other one is used for spiking and recovery testing. Adjust the pH of each aliquot to 2 $\pm$ 0.5 with approximately 1 mL of 1:1 HNO_3. Shake carefully to release carbon dioxide. Add 1.0 mL of diphenylcarbazide solution, and dilute to the mark with water. Allow the solution to stand for about 10 minutes, then transfer to an absorption cell and measure the absorbance at 540 nm using water in the reference cell. If the absorbance of the sample exceeds the highest standard (40 μg Cr^{6+}) as determined in Section 3.9, pipet an aliquot into a volumetric flask, and dilute to the mark with water. Dilute the 0 μg standard by an equivalent amount

to obtain a blank for that sample. Subtract the 0 μg standard reading (**not** the field blank) to obtain the net absorbance of the sample. Measure the blank train using the same aliquot sizes and dilutions as above, and subtract the reagent blank to determine the net absorbance of the blank train.

Check for matrix effects on the Cr^{6+} results. Since the analysis for Cr^{6+} by colorimetry is sensitive to the chemical composition of the sample (matrix effects), check at least one sample from each source point using the method of standard additions as follows: Spike the reserved aliquot with an aliquot of standard solution that increases the Cr^{6+} concentration by at least 50 percent (or to a minimum of 10 μg) and analyze the sample as described in the paragraph above. Calculate the Cr^{6+} mass (in μg) in the aliquot of the unspiked sample solution by using equation 3.8.1 in Section 3.8.

Volume corrections will not be required since the solutions as analyzed have been made to the same final volume and dilution. If the results of the method of standard additions procedure used on the single source sample do not agree to within 10 percent of the value obtained by the routine spectrophotometric analysis, then reanalyze all samples from the source using the method of standard additions.

3.7.2 Analysis for Hexavalent Chromium by IC Method

Any sample that yields an absorbance of less than 0.010 by the DPC method must be analyzed for hexavalent chromium by the IC method.

The IC must first be calibrated as described in Section 3.9.2. Then, using the same sample volumes and instrument parameters, analyze the samples, blank trains, spikes and check standards (described in Section 3.10.2). If any sample exceeds the highest standard, it must be diluted with eluent so that it

falls on the calibration curve. Complete the run with a final calibration curve, and evaluate the whole analysis as described in Section 3.10.2.

The following specific instructions are given for the Dionex IC pre concentration mode. Consult manufacturer's operating manuals for other instruments or direct injection made.

Convert Dionex IC to the sample preconcentration mode by replacing the sample loop with a preconcentrator column.

Fill the post-column reagent and eluent reservoirs and verify that the power and compressed air are on. Degas the post-column reagent by bubbling helium through it for 10 minutes, and cover the reservoir. Turn on the detector power, set the filter wheel to 520 nm (No. 4). Turn on the eluent pump, and measure the eluent flow at the waste line using a 5 mL graduated cylinder and stopwatch. The

flow should be 0.9 mL per minute. If not, adjust the flow by using the dial on the eluent pump.

Turn on the post-column reagent pump and measure the total flow at the waste line. The total flow should be 1.2 mL per minute. If not, adjust the flow by using the flow control dial on the post-column reagent pump.

Place the sample inlet line in water, switch to "inject", and turn on the sample pump for a few minutes. This flushes the side loop and sample pump with water. Then turn the pump off.

Place the sample inlet line in an accurately known volume of sample. Switch to "load" and immediately turn on the sample pump. When the liquid is almost gone (**CAUTION! Do not let air get in the line**) add enough water to allow pumping for an additional 10 minutes. This loads the entire sample onto the concentrator column. Turn off the pump and switch the valve to "inject". This will begin to

pump eluent through the concentrator column onto the analytical column. Following elution of the peaks, flush the side loop and sample pump with water as previously described before loading another sample or standard.

3.7.3 Total Chromium by Atomic Absorption

a. Digestion for Analysis by Atomic Absorption

The portion of the sample intended for atomic absorption analysis must first be subjected to an acid digestion procedure. This is necessary to convert organic forms of chromium to inorganic forms, to minimize organic interferences, and to convert the sample to a suitable solution for analysis. Both the remainder of the sample from the hexavalent chromium analysis and the final sample train acid rinse are analyzed for total chromium. However, they are digested and analyzed separetely because each portion represents different aliquots.

Add 10 mL of concentrated HNO_3 to each sample bottle and allow to stand for an hour. Shake and transfer each solution to separate beakers, rinsing the bottles with 1:1 HNO_3. Evaporate the samples on a hot plate to near dryness. Add another 10 mL of concentrated HNO_3 to each beaker, wetting the sides of the beaker with acid. Place the beakers on a hot plate and reflux the sample down to approximately one milliliter.

Wash down the beaker walls and watch glass with water and filter the samples, only if necessary, to remove silicates and other insoluble material that could clog the nebulizer. If filtration is necessary, use an all-plastic and glass system that has been washed with 1:1 HNO_3. Samples may also be allowed to settle; liquid for analysis may be decanted gently. Adjust the volume to exactly 50 mL or to a predetermined value based on the expected metal concentrations. Store

in pre-cleaned polyethylene bottles until analysis.

Digest the solutions recovered from the blank train using the same procedure as above.

b. Analysis for Total Chromium by Flame-AAS

The digested samples and blank are then analyzed for chromium by flame-AAS, using a nitrous oxide-acetylene flame.

The manual supplied by the manufacturer should be consulted for the spectrophotometer parameters and operating instructions.

The 357.9 nm wavelength line is the most sensitive for chromium, and yields acceptable results up to a concentration level of 50 μg/mL. When higher concentrations are encountered, use less sensitive wavelengths, (e.g. 425.4 nm, 428.9 nm, 520.8 nm, and

520.4 nm), instead of diluting the sample.

At least three readings should be obtained and averaged for each measurement.

The instrument is calibrated using the procedure in Section 3.9.3.

Calculate the mass of chromium in the unspiked sample using Equation 3.8.3.

c. Analysis for Total Chromium by Furnace-AAS

If the flame-AAS analysis yields an absorbance less than 0.100, use furnace-AAS to analyze.

Use the 357.9 nm wavelength line for total chromium analysis by furnace-AAS.

Follow the manufacturer's operating instructions for all other spectrophotometer parameters.

Calibrate the instrument as in Section 3.9.4.

Inject a measured μL aliquot of sample into the furnace and atomize. If the measured concentration is greater than the highest standard as determined in Section 3.9.4, the sample should be diluted in the same acid matrix and reanalyzed. The use of multiple injections can improve accuracy and help detect furnace pipetting errors.

Analyze the blank train using the same procedure.

Check for matrix effects by spiking at least one sample per source point, and analyzing as above. During the analysis, inject a midpoint (check) standard after every set of injections or ten injections, and then a blank, to check for instrument drift and sensitivity. Calculate the mass of chromium in the unspiked sample using equation 3.8.4.

3.8 Calculation and Reporting

Report Cr^{6+} and total chromium to the nearest 0.1 μg for both the train and the field blank. Calculate the results as follows:

3.8.1 Calculation for Hexavalent Chromium (Cr^{6+}) by DPC Method

$$\mu g\ Cr^{6+} = A_{spl} \times R \times AF \times D$$

where:

A_{spl} = Absorbance of sample corrected for reagent blank, at 540 nm

R = Response factor of the instrument, μg Cr^{6+} per absorbance unit (Section 3.9.1)

AF = Aliquot factor of this analysis

D = Sample dilution needed to bring absorbance into instrument range (if used)

3.8.2 Calculation for Hexavalent Chromium by IC Method

$\mu g\ Cr^{6+}$ = C x AF x D

where:

C = Concentration of sample ng/mL, (usually computed by the instrument)

AF = Aliquot factor of this analysis

D = Sample dilution needed to bring sample into the range of the calibration standards (if this dilution needed)

3.8.3 Calculation for Total Chromium by Flame-AAS Method

$\mu g\ Cr$ = C x D x V x AF

where:

C = Concentration of sample µg/mL (usually computed by the instrument)

D = Sample dilution needed to bring reading into instrument range, (if used)

V = Volume of digested sample, mL (usually 50 mL)

AF = Aliquot factor

The total amount of the recovered sample divided by the portion of it used for the digestion, which is normally the remainder of the solution not used for hexavalent analysis.

3.8.4 Calculation for Furnace-AAS Method

µg Cr = C/1000 x D x V x AF

where:

C = Concentration of sample in ng/mL, (usually computed by the instrument)

D = Sample dilution needed to bring reading into instrument range (if used)

V = Volume of digested sample, mL (usually 50 mL)

AF = Aliquot factor

The total amount of the recovered sample divided by the portion of it used for the digestion, which is normally the remainder of the solution not used for hexavalent analysis.

3.8.5 Calculation for Spiking

3.8.5.1 Hexavalent Chromium by DPC Method

$$\mu g\ Cr^{6+} = \frac{(m)\quad A_{spl}}{(A_{spk} - A_{spl})}$$

where:

m = Mass of spike, μg

A_{spl} = Absorbance of sample corrected for reagent blank

A_{spk} = Absorbance of spiked sample corrected for reagent blank

3.8.5.2 Hexavalent Chromium by IC Method

$$\mu g\ Cr^{6+} = \frac{(m)\quad C_{spl}}{(C_{spk} - C_{spl})}$$

where:

m = Mass of spike, μg

C_{spl} = Concentration of sample, $\mu g/mL$

C_{spk} = Concentration of spike, µg/mL

3.8.5.3 Total Chromium by Atomic Absorption Methods

$$\mu g\ Cr = \frac{(m)\quad(C_{spl})}{(C_{spk} - C_{spl})}$$

where:

m = Mass of spike, µg

C_{spl} = Concentration of sample, µg/mL

C_{spk} = Concentration of spike, µg/mL

3.9 Calibrations

3.9.1 Calibration for Hexavalent Chromium by DPC Method

Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using

an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute for Standards and Technology (NIST), (formerly the National Bureau of Standards). Specific details on the use of such materials should be supplied by the vendor. General information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer must read correctly within ± 5 nm at all calibration points; otherwise, the spectrophotometer must be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 540 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.

Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a

double-beam spectrophotometer, scan the spectrum between 530 and 550 nm using a 50 μg Cr^{6+} standard dilution in the sample cell and a blank solution in the reference cell. If a peak does not occur, the spectrophotometer is malfunctioning and should be repaired. When a peak is obtained within the 530 and 550 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of observance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum difference in absorbance between the standard and the blank occurs.

Pipet 0, 1, 5, 10, 20, and 40 mL of dichromate intermediate solution (1 mL = 1 μg Cr^{6+}) into 50 mL flasks. Acidify each to pH 2.0 ± 0.5 with 1:1 HNO_3. Add 10 mL of DPC and dilute to exactly 50.0 mL with water. This corresponds to 0, 1, 5, 10, 20, and 40 μg of Cr^{6+}. Use water in the

reference cell and subtract the 0 mL standard from each reading to obtain corrected absorbance.

Calculate the least squares slope of corrected absorbance versus micrograms to determine the response factor (R) of the procedure. Standard additions must be used to determine sample concentration if matrix effects are significant, as determined in Section 3.7.1. In this case, plot added concentration versus absorbance, and extrapolate the curve to the X-axis to obtain sample concentration.

3.9.2 Calibration for Hexavalent Chromium by IC Method

a. Inject a five-point series of Cr^{6+} standards diluted in eluent reagent in the range of interest. The concentration of the highest standard should be no more that 10 times the lowest standard. Standard concentrations must bracket sample concentrations.

b. Determine the least squares fit. The calibration data should result in a correlation coefficient of 0.995 or better.

3.9.3 Calibration for Total Chromium by Flame-AAS Method

a. Aspirate a series of three chromium standards diluted in 2.5 percent HNO_3 in the appropriate concentration range. The lowest standard should be selected to give an absorbance of about 0.1. Make three readings for each.

b. Construct a calibration curve by plotting absorbance values against micrograms of chromium per milliliter, and calculate the regression line. (Instruments that read directly in concentration handle this internally.)

3.9.4 Calibration for Total Chromium by Furnace-AAS Method

Either (1) run a series of chromium standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) for the method of standard additions, plot added concentration versus absorbance. For instruments that read directly in concentration, use the curve corrector to read out the proper concentration. Calibration curves must be composed of a minimum of one blank and three standards.

Check furnace parameters as provided by the manufacturer to determine whether temperature sensitive calibrations have drifted. Confirm these parameters by systematically altering the furnace parameters while analyzing a standard. In this manner, losses of analyte due to higher than necessary temperature settings can be minimized while maintaining optimum sensitivity.

3.9.5 Balance Calibration

Calibrate balances against NIST traceable weights.

3.9.6 pH Meter Calibration

Calibrate the pH meter using a two-point procedure that spans the pH of interest, following manufacturer's instructions.

3.10 Quality Control

3.10.1 Gravimetric

Reweigh one impinger per set or one in ten, whichever occurs first, at each step. If the second weight is not within ± 0.5 g of the first, check the balance calibration, and reweigh the entire set.

3.10.2 Quality Control for Hexavalent Chromium by DPC Method.

Compare instrument response factor and blank against previous results. A significant change (more than 10 percent) may indicate deterioration of diphenylcarbazide, instrument wavelength

drift, or other problems. Investigate the problem until calibration results are close to expected. Analyze one midrange standard made from dichromate obtained from a different source than the standard with each set of samples or every ten samples. Results must be within ± 10 percent of expected. If not, void the previous results and investigate the procedure until it is under control, then reanalyze the samples. Procedures for field blanks and spiking which are included in the procedure, comprise most of the analytical QC measures required for this analysis.

3.10.3 Quality Control for Hexavalent Chromium by IC Method

When preparing a new stock solution, prepare the midpoint calibration standard from the old and the new stock. Analyze the old and the new standards and compare the responses, which should agree within five percent.

Run a spiked sample every 10 samples, or every set of samples, whichever occurs first. Choose a sample that represents actual emissions (an outlet sample, for instance) where possible. The spike should approximately double the sample concentration. Run a midpoint check standard at least every tenth sample. Also run a known concentration that has been prepared from another source of hexavalent chromium. The analytical run should be completed after an additional ten samples with another calibration curve. If the peak heights of any of the standards change more than ten percent or the control differs by more than ten percent from expected, the samples should be rerun.

3.10.4 Quality Control for Total Chromium by Flame-AAS Method

During the analysis, aspirate a blank and a midpoint standard as a check after every set of samples, or at least every ten samples, to check for instrument drift and sensitivity. If the check shows variance

exceeding five percent, the previous samples must be reanalyzed.

Check for matrix effects by spiking at least one sample for each source point, choosing an outlet sample rather than an inlet. The spike should be at least 50 percent of the chromium in the sample, or five micrograms, whichever is larger. Calculate the measured mass of chromium in the spiked sample using the equation in Section 3.8.5.3. If the spike is not recovered within ten percent, then all the samples from this source should be reanalyzed using the method of standard additions to eliminate the matrix effect.

3.10.5 Quality Control for Total Chromium by Furnace-AAS Method.

Run a check standard after every set of injections or ten injections, whichever occurs first. A significant change in response (more than 10 percent) may indicate graphite tube deterioration or other problems. In case of a significant change in response, stop the analysis and

investigate the problem until the analysis is under control, then reanalyze the samples. Follow the check standards with a reagent blank to confirm that no "memory effects" are occurring.

Verify the concentration of the standards against one other standard obtained from an outside source.

Procedures for field blanks and sample spiking which are embedded in the procedure comprise most of the analytical QC measures required for this analysis.

DETERMINATION OF HEXAVALENT CHROMIUM AND TOTAL CHROMIUM EMISSIONS FROM CHROME PLATING AND ANODIZING EQUIPMENT USING A WET IMPINGEMENT TRAIN

4. Engineering Calculations

4.1 Sample Volume (Standard)

Correct the sample volume measured by the dry gas meter to standard conditions 15°C (60°F) and 760 mm Hg.

$$V_{m(std)} = V_m Y[(T_{std}/T_m)\ (P_{bar}/P_{std})]$$

where:

$V_{m(std)}$ = Volume at standard conditions of gas sample through the dry gas meter, dscm

V_m = Volume of gas sample through the dry gas meter at meter conditions, m^3

T_{std} = Absolute temperature at standard conditions, 288°K

T_m = Average absolute dry gas meter temperature, °K

P_{bar} = Barometric pressure at the sampling site, mm Hg

P_{std} = Absolute pressure at standard conditions, 760 mm Hg

Y = Dry gas meter calibration factor

4.2 Concentration of Cr^{6+} and Cr(Total)

Calculate the concentration of Cr^{6+} and Cr(total) in the gas stream at standard conditions using the following equation:

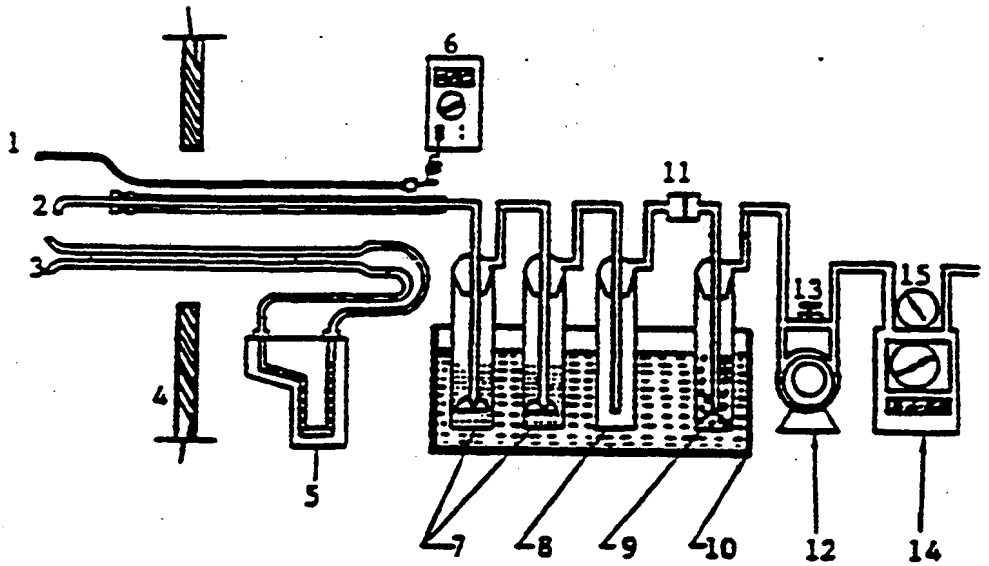
$$Cr^{6+} \text{ or } Cr(total) = m_{ch}/V_{m(std)}$$

where:

Cr^{6+} or Cr(total) = Concentration of Cr^{6+} or Cr(total) at standard conditions, μg/dscm

m_{ch} = Mass of Cr^{6+} or Cr(total) reported by the laboratory, μg

$V_{m(std)}$ = Total sample volume at standard condition, dscm



1. Temperature Sensor
2. Glass Probe and Nozzle
3. S-Type Pitot Tube
4. Stack Wall
5. Inclined Manometer
6. Temperature Sensor Meter
7. Impingers with 100 mL 0.02N $NaHCO_3$
8. Empty Bubbler
9. Bubbler with Tared Silica Gel
10. Ice Bath
11. Back-Up Filter (Teflon)
12. Sealed Pump
13. By-Pass Valve
14. Dry Gas Meter
15. Temperature Gauge

Figure 205.1-1

CHROME IMPINGER TRAIN SET-UP